Analysis of Phthalates in Food Contact Materials

Selected samples from the Norwegian Market

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By
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Preface

This investigation was planned in cooperation with Julie Tesdal Håland, Mattilsynet, section “Fremmedstoffer og EØS». Samples were taken in Region Stor-Oslo.
Analysis and reporting was performed by Lisbeth Krüger Jensen and Jens Højslev Petersen at the National Food Institute. Vibeke Balswel was assisting in the laboratory work.

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Content

Summary

Samples suspected to contain phthalates like DEHP and DBP were taken of drinking equipment sold from a Norwegian retail shop with party novelties. Substances used in food contact plastics should only contain additives, like plasticisers, that are authorised and the migration into food or relevant food simulants must be below certain migration limits. Unfortunately, half of the samples contained non-authorised plasticisers and the other half showed too high migration of authorised phthalates. Furthermore, the quality of compliance documentation was very low and did not fulfil the legal requirements.

1. Background

In 2014 a joint Nordic control campaign about the quality of Declarations of Compliance (DoC) for Food Contact Materials (FCM) including analytical control of phthalates in selected FCM for fatty foods was performed. That campaign was financed by the Nordic Council of Ministers. In Norway some extra samples, also suspected to contain phthalates, were taken of drinking equipment sold from a retail shop with party novelties.

2. Regulation of phthalates in plastic FCM

Additives like phthalates have been risk assessed by the European Food Safety Authority before being listed and authorised in annex 1 of the FCM plastic regulation (the positive list). Manufacture and import into the European Community of plastic materials and articles intended to come into contact with food, not complying with the restrictions and specifications for Dibutyl phthalate (DBP), Butylbenzylphthalate (BBP), Di- (2-ethylhelhyl)phthalate (DEHP), Di-isononylphthalate (DiNP) and Di-isodecylphthalate (DiDP) was prohibited since 2008 (EU regulation 2011). In some cases the phthalates used in FCM are regulated by compositional limits (hereafter referred to as Quantum Maximum (Qm)) in others by specific migration limits (SMLs). The interpretation of the restrictions are not easy and was therefore explained more in details in a guideline from the EU reference laboratory for FCM (Hoekstra et al., 2011). A simplified table of the critical parameters to control in enforcement is shown in Table 1.

Table 1. Regulation of "classical" phthalates in the plastics regulation (EU 10/2011): Survey of the critical parameters to control in enforcement work.

		SML	Qm	Parameter to control in single use Food Contact Material			Parameter to control in repeated use Food Contact Material		
PM-no	Substance	(mg/kg food simulant)	(% in the plastic)	Fatty food	Infant food	Non-fatty food	Fatty food	Non-fatty food	Infant food (non-fatty)
74560	Phthalic acid, benzyl butyl ester (BBP)	30	0.1	Qm		SML	SML		
74640	Phthalic acid, bis(2-ethylhexyl)ester (DEHP)	1.5	0.1	Qm			Qm	SML	
74880	Phthalic acid, dibutyl ester (DBP)	0.3	0.05	Qm			Qm	SML	
75100	Phthalic acid, diester with C8-C10 (DiNP)	9 (SML(T) incl. DiDP)	0.1	Qm		SML	SML		
75105	Phthalic acid, diester with C9-C11 (DiDP)	9 (SML(T) incl. DiNP)	0.1	Qm		SML	SML		

A few other phthalates not present in Table 1 were seen in this investigation. Di-isobutylphthalate, which from time to time is found in plastics, has not been assessed by EFSA and is therefore not on the positive list. In practice the detection limit for this substance in plastic is about the same as for DBP. Another type of phthalate, which is not being investigated further here, Di-(2-ethylhexyl)*tere*phthalate (DEHT), is authorised with an SML of 60 mg/kg.

Control of migration limits for phthalates should be performed with the official food simulants. This is because of the risk that the food may already be contaminated with phthalates from the external and/or internal environment before the contact with the FCM occurs. Only when the phthalate concentration in the foodstuff is well known before being brought into contact with the FCM, a minor violation of the present SML's in foods could be used as the basis for a case in court. However, sanctions will of course still be applied to higher phthalate concentrations in the foodstuff, which according to the regulation is considered harmful to health in a specific risk assessment.

3. Analysis of phthalates

Overview: During inspection of the enterprise, samples were taken for analytical control of compliance with legislation. The food inspector did send samples of soft plastic to the laboratory together with the DoC and any other documents available containing eventual information about restrictions in use for the FCM. The following procedure was used in the laboratory:

1) Identification of the plastic polymer.

2) Determination of the phthalate concentration in the plastic, if any (Method FA411.1).

3) Study of declared area of use with respect to food type, contact time and temperature. Was it a FCM for single or repeated use?

4) If relevant, determination of migration after one or three migration tests from the FCM to a food simulant (50% ethanol in water) during realistic exposure conditions (Method FA413.2).

5) Conclude from the test results if samples were compliant or not

Finally a certificate with the result and an assessment of the result was send to the food inspector.

3.1 Sample material

In the winter 2015 four samples (figure 1) were taken by a food inspector from Mattilsynet according to an agreed scheme including an interpretation of the legislative text (Table 1). Specifications were given about size and number (seven) of items per sample. Sampling was performed at a retailer, Teknikmagasinet, Byporten Shopping, Jernbanetorget 6, 0154 Oslo, selling FCM novelties. The inspector was encouraged to collect and investigate all relevant documentation available including declarations of compliance and any supporting documentation.

For two of the samples it turned out that not all items belonged to the same batch. Therefore, in practice a total of six samples were analysed.

Figure 1: Samples included in the investigation: Drinking glasses (K15-0014), Drinking hat (K15-0015a+b), Big beer bong (K15-0016a+b) and Small beer bong (K15-0017).

3.2 Chemicals, laboratory equipment and procedures used

A summary is presented here but all details on materials and methods are available elsewhere (Petersen and Jensen, 2010).

To avoid problems in the analyses, utility items and solvents used were of high purity and blank values of phthalates were carefully controlled. Further all glassware was heated overnight at 450°C before use.

The following standard substances of high purity were used: Di-isobutylphthalate (DiBP, CAS nr 84-69-5), Di-butylphthalate (DBP, CAS-nr. 84-74-2), Butyl-benzylphthalate (BBP, CAS-nr. 85-68-7), Di-ethylhexylphthalate (DEHP, CAS-nr. 117-81-7), Di-isononylphthalate (DiNP, CAS no 28553-12-0 or 68515-48-0), Di-isodecylphthalate (DiDP, CAS no 68515-49-0 or 26761-40-0). Deuterium labelled substances used as internal standards were: Ring-D4-DnBP; 3,4,5,6 Ring D4-BBP; Ring D4-DEHP; 3,4,5,6 Ring D4-DnOP and 3,4,5,6 Ring D4-DnNP.

For identification of plastics attenuated total reflectance Fourier Transform InfraRed (FTIR) spectra were recorded and compared to a digitalised polymer library (Spectrum One, Perkin Elmer).
Following method FA411, samples of PVC were easily dissolved. Extracts of dissolved and precipitated plastic was cleaned by centrifugation in a Hereaus Megafuge.

In the case of sample K15-0015, part of the hoses was intended for immersion into a bottle of beverage placed on top of the drinking hat. This hose was tested by total immersion. Sample K15-0017 was tested by filling since it was intended to be placed on top of a bottle.

Phthalates present in extracts from plastics and in food simulants was determined by gas chromatography (Agilent 6890A) with electron ionisation and mass selective detection (Agilent 5973). One ion was used for quantification and two others for verification of identity (qualifier ions).

3.3 Test conditions

Selection of test conditions for samples which has to be tested for migration is specified in the regulation (EU 10/2011). In this project, only two samples of plastic, which could be used for milk products, juice and beverages with or without alcohol was considered. Here the food simulants of choice are simulants A, C and D1, which are ethanol/water mixtures. Among these, the food simulant for milk and juice, 50% ethanol/water is the more severe for phthalates in PVC. Time and temperature conditions were selected from EU regulation 10/2011. It was believed that the contact time could be more than one hour and that contact would take place at ambient temperature. In both cases the test conditions were 2 hours@40°C repeated three times on three different days. Only the third portion of food simulant was analysed. The concentration, which was to be compared to the migration limit, was calculated using the “6 dm^2 per kg food” convention since the volume of the hoses were below 500 ml.
The migration modelling software was Migratest Lite (with update 2002, FABES GmbH, Munich, Germany).

3.4 Quality assurance

The Danish accreditation body (DANAK) supervise the methods applied in DTU-Food, Department of Food Chemistry, also those applied for the determination of phthalates in plastic and in food simulants. Routines are established for daily quality control of the methods taking into consideration a suitable composition of the analytical assays with respect to the number of

samples that are analysed in multiplicity, laboratory/solvent blanks and known samples for the control chart.

4. Results and discussion

The food inspector was asked to take samples of soft plastics, preferentially from polyvinyl chloride (PVC), expected to contain a high concentration of plasticisers. All samples were produced in China and were repeated use articles. A survey of the samples taken for analytical control in the enforcement campaign is shown in table 4.1.

Table 2. Hoses from different types of drinking equipment analysed for content of phthalates.

Sample type	DTU Sample no.	Tradename	DoC with restrictions about time, temp and food type when in use	Phthalate concentration in plastic (%)		Phthalate concentration in food simulant after all surface/volume correction (mg/kg)		Comments about possible non-compliances
				DBP	DEHP	DBP	DEHP	
Hose (from spectacles)	K15-0014	Drinking glasses (spectacles) with hose	No	n.d.	n.d.	-	-	High concentration of unknown, not authorised phthalate. Possibly isodecylphthalate
Hose (from white hat)	K15-0015a	Drinking hat	No	2.0	0.07	20.2 (16.5-23.8)	n.d.	Migration of DBP > 0.3 mg/kg
Hose (from blue hat)	K15-0015b	Drinking hat	No	n.d.	n.d.			
Hose with funnel (green hose)	K15-0016a	Big beer bong	No	0.05	0.06			Contains about 25% DiBP, which is not authorised
Hose with funnel (slightly blue hose)	K15-0016b	Big beer bong	No	n.d.	n.d.			
Hose	K15-0017	Small beer bong	No	0.81 (0.69-0.93-0.82)	25.2 (24.2-25.1-26.4)	19.8 (20.8-17.2-21.4)	70 (76.1-64.4-70.8)	Migration of DBP and DEHP above migration limits of 0.3 and 1.5 mg/kg respectively.

The analysis verified that all hoses were made from PVC. Several of the samples contained significant amounts of the plasticiser Di-(2ethylhexyl)-*tere*phthalate (DEHT). It was not a part of this project to test migration of this substance.

Sample K15-0014 did not contain any of the phthalates, which were targeted. But an “unknown” belonging to the family of phthalates was found in huge amounts. From the mass spectrum it was concluded that in all probability it was an isomer of isodecylphthalate, which is not on the positive list. Therefore the sample is non-compliant.
One sample (number) was supposed to be consisting of seven identical items from the same batch. However in two of the four samples, K15-0015 and K15-0016, they were not.
From the appearance of the drinking hat items it could be seen that the hats did differ in colour. However, it was not visible that the hoses also differ in composition, which was actually the case (Sample K15-0015 a+b, Table 2). The hose from the white drinking hat (named sample 0015b) contained 2% DBP and, in a migration test, turned out not to be compliant with the migration limit of 0.3 mg/kg (Table 1).

The colour of the hoses used in the big beer bong differed in colour and so did the plasticiser composition (Figure 1 and Table 2). By comparison with the pure substance, it was concluded from the mass spectrum that the primary plasticiser in the green hose of sample K15-0016a was Di-isobutylphthalate (DiBP). Unfortunately, this phthalate is not on the positive list and the sample therefore non-compliant. Sample K15-0016b complied with limits in table 1.
The last sample, K15-0017, contained DBP as well as DEHP in high concentration. In a migration test both substances migrated in amounts high above the limits: 66 times the limit for DBP and 47 times the limit for DEHP.
One could argue that other and milder test conditions than 2 hours at 40°C should have been used for sample K15-0017. However, even if the shortest test time of 5 minutes was chosen from the table in annex V of EU Regulation 10/2011 the sample would have been non-compliant. A typical example of the kinetics of the migration in a hose with the same dimensions as the bong was produced with the migration modelling software and is shown in Figure 2.

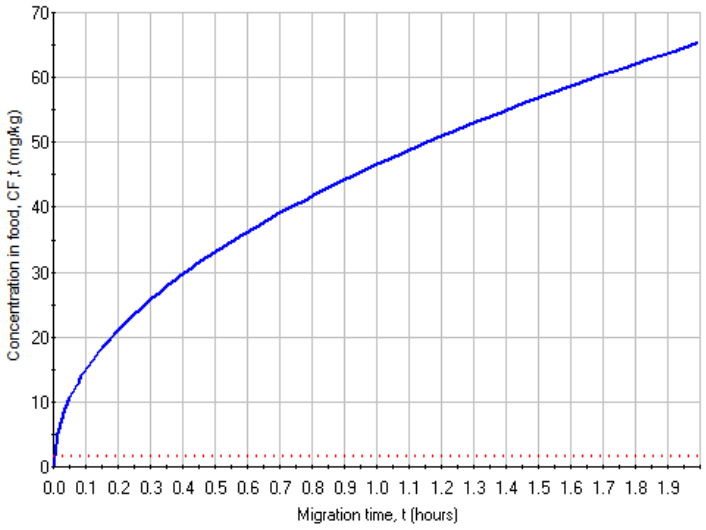

Figure 2: Theoretical and fitted migration curve for a substance with same molecular weight as DEHP from a plasticised polymer into a food simulant where it has limited solubility. Red line illustrates a migration limit of 1.5 mg/kg.

It is clear from figure 2 that when the migration is as high as 65 mg/kg after two hours, the migration is about 10 mg/kg after only 3 minutes. However, it must be stressed that this calculation contains much uncertainty.

In all instances DoC was not of satisfactory quality for selection of the appropriate area of use. Where supporting documentation was provided the traceability to the actual sample was doubtful.

5. Assessment and Conclusion

All samples of drinking equipment showed non-compliance with the legislative limits for phthalates in plastics for Food Contact. Only some single items from the inhomogeneous batches of samples were compliant (with respect to phthalates).
The quality of compliance documentation was very low and did not fulfil the legal requirements.

6. References

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